

Coupling of Long-Range Critical Fluctuations and Short-Range Solvation

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The existence of critical effects upon the solvation of attractive solutes has been a matter for debate. The relevant question is if the presence of long-range critical fluctuations can modify the short-range solvation shell around a solute. Experimental information, gathered using pure solvents close to the vapor–liquid critical point, has been rather inconclusive, as the difficulties that plague this thermodynamic region (due to the large compressibility and expansivity) preclude the precise control of the system. We have developed a new strategy consisting of studying the changes in the solvation shell of probe molecules dissolved in a binary *solvent mixture* close to its lower *consolute critical point*. The study is based on UV–vis absorption and steady-state fluorescence emission measurements of the solvatochromic and thermochromic effects of two dyes dissolved in mixtures of lutidine–water. The results show unambiguously the existence of a subtle change in the composition of the near-critical solvent surrounding the probe molecules with respect to the bulk composition, thus indicating a coupling of long-range critical fluctuations with short-range intermolecular interactions. Solvation dynamics in near-critical conditions is also discussed.